

## **SOUTHERN CALIFORNIA PARTICLE SUPERSITE**

**Progress Report for Period July 15-November 1 2000**

**United States Environmental Protection Agency**

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### **1. Introduction**

The research activities of our Southern California Supersite (SCS) are integral part of the overall themes of the Southern California Center for Ambient Particulate Matter (SCCAPM), a 5-year program that we were awarded through EPA's STAR initiative approximately one year ago

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution chemical composition and physical state, spatial and temporal variability and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). The specific research objectives are:

1. To characterize PM, its constituents and precursors, to better understand sources and transport affecting human exposure and to support development of State Implementation Plans (SIPs).
2. To obtain atmospheric measurements to support health studies designed to address causal factors, etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways.
3. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM including evaluation of new instrumentation, sampling methods and federal reference methods.

This report addresses the period between July 15 to November 1, 2000.

## **2. Particle Instrumentation Unit (PIU)**

### **GENERAL PIU STATUS AND PROGRESS**

- 1) PIU 20-foot trailer was transported to Ranchos Los Amigos Laboratory, Downey, Los Angeles County (August 3) – first, of a minimum of five, for the Supersite project.
- 2) Two 50amp, 120 Volt Power conduits connected to trailer, September 15. Transformer installed to reduce 480 Volt from MRI supply unit to 120 volts for trailer. Temporary Extension cords were connected to trailer between Aug 3 and September 15 to calibrate instruments and to conduct preliminary characterization of the Downy environment – as part of the completion of the scheduled characterization for Warren Hall, UCLA.
- 3) Interior walls and shelves of trailer painted with primer and 2 coats of semi-gloss during mid-August.
- 4) Site security items addressed:
  - A) Adding a security door to the ladder (to deter vandalism)
  - B) Installation of chain tire locks for both 10 and 20 foot trailers (to deter vandalism), and
  - C) Installing concrete parking barriers along the electrical conduit outside the trailer to deter hospital patients from walking and tripping over conduit.
- 5) Installation of functional items such as mini blinds to block sunlight from instrument and to maintain indoor air temperature
- 6) Mini Refrigerator installed for temporary storage of filters between period to drive or ship them to analytical lab.
- 7) Size-selective inlets with rain hats for each instrument in the design and testing phase. Previous published empirical and theoretical results used to estimate particle penetration and droplet cut-off efficiency. Most important for continuous and 24-hour integrated impactor samplers that measure coarse particles (e.g., APS and MOUDI's).
- 8) Pump Boxes: Three pump enclosures have been designed by Dr. Hinds, and built by UCLA Machine shop, able to handle two medium size 1/3 HP MOUDI pumps, or 3 smaller pumps (e.g., for TEOM or Aethalometer). Enclosures serve to baffle noise, reduce transmission of mechanical vibration, and to protect pumps from exposure to condensation and precipitation. Pump enclosures are locked shut, located under PIU trailer, and chain-locked to trailer frame.

- 9) Solenoid system installed within each pump enclosure to switch on coupled cooling fan that is activated by individual pump or all pumps within an individual enclosure. Power switches for individual pumps are located near their respective samplers inside the trailer.
- 10) Filter handling and weighing protocol for MOUDI and Partisol was developed and implemented. Methods to transport filters to and from the PIU is under way. Filter and other climate sensitive samples are transported in an ice cooler. A HOBO data logger, which records Temperature and Humidity at 5 minute intervals, is co-located with the samples throughout there life-time in the field.
- 11) SOPS: Internal draft prepared (2 copies): describes general operation procedures for particle monitors, meteorologic al/climate monitors, and contains other general trailer records and procedures: original version in trailer; and copy one in lab.
- 12) Met-One Wind Tower in construction phase. Rhom triangular tower (10 meters). Hinge-plate being designed to be attached to tongue of 20 foot PIU trailer.

#### LIST OF CONSTRUCTION ITEMS TO BE COMPLETED BY ON-SITE HANDYMAN

1. glass sampling manifold for gas monitors
2. Add drain to A/C
3. Thermostat: for coupled control of floor heaters and A/C.
4. Installation of 10-meter Rohn tower for Met-One wind van.
5. Possibly, improve on the roof ladder security door.
6. Construction of anti-vibration sound absorbing ventilated compartment in wheel well for smaller instrument pumps.

#### OPERATION STATUS /PROGRESS OF PIU TRAILER & GENERATION OF RESEARCH DATA

- 1) All particle monitors continue to be in operating condition. As of September 15 routine continuous monitoring conducted with TEOM, Aethalometer, SMPS, APS, and DataRAM. Time-integrated intensive 24-hour measurements using 3 MOUDIs compared to Partisol Plus Dichotomous sampler. Sampling scheme is as follows:
  - A) Tuesday's
    - i) Rotating MOUDI-A with Al-foil Substrate for EC/OC analysis.

ii) Rotating MOUDI-B with Teflon substrate for Elemental analysis

B) Thursday's

i) Non-Rotating MOUDI-A with Teflon substrate for PAH analysis as a control.

ii) Non-Rotating MOUDI-B with Teflon substrate for PAH analysis, including:

(1) an upstream denuder to remove semi-volatile particle associated PAHs, which may positively contribute to artifact formation on the filter sample, and

(2) a downstream PUF filter to remove semi-volatile particle associated PAH's that may be released from sampled particles - under the low-pressure conditions of the lower stages of the MOUDI.

- 2) TEOM study for continuous coarse particle monitoring system. In characterization phase: using virtual impactor (VI) to prevent more than 90% of particles less than 2.5 microns from penetrating, and an elbow nozzle, upstream of the VI, to prevent particles larger than 10 microns from penetrating.
- 3) SMPS/APS 24 hour continuous monitoring of ambient air particle size distributions.
- 4) Partisol monitoring during PAH/MOUDI, and TEOM study to compare data sets (paired),
- 5) Aethalometer 24 hour continuous monitoring of ambient elemental carbon and "qualitative" PAH's.
- 6) DataRAM - measuring continuous particle mass below 2.5 microns.
- 7) Data Management plan in progress (see Appendix, below). Analogue signal data logger for a) Met-One Wind System and b) Vaisala ambient and indoor-trailer Thermo-hygrometer received and being installed. Multi-port Digital 8-port RS232 adapter card acquired and in the process of being installed.

PIU Detailed Status and Progress: Continuous Monitoring Instruments

	INSTRUMENT (Model)	STATUS / PROGRESS
1	<b>SMPS (Model 3934, TSI Inc.);</b>	Calibration of SMPS and APS with mono-disperse PSL particles. The SMPS was mono-disperse PSL particles of size 0.03µm, 0.21µm and 0.67µm respectively. They were purchased from Bangs laboratories, Inc. (Fisher, IN) and generated by using a generator (BGI, Inc., Waltham, MA). The particle sizes indicated by the SMPS were exactly labeled by the company.
2	<b>APS (Model 3310, TSI Inc.)</b>	The APS was calibrated with mono-disperse PSL particles of size 0.67µm and 3.6µm. The particle sizes indicated by the APS were one channel smaller than those labeled. After the total sampling flow of the APS was measured, it was found the actual flow was less than the instrument indicated. This may explain the discrepancy of measured particle flow was adjusted thereafter.
3	<b>DataRAM, Mie Inc.</b>	Sampling Continuously
4	<b>TEOM Model 1400, R&amp;P, Inc.</b>	Set-up for sampling ambient air through PM10 inlet. Intensive study to develop a calibration curve for particle monitor, using a Virtual Impactor (VI) as a size-selective inlet (< 10% of 2.5µm penetrate), and upstream elbow nozzle to prevent 10 micron particles from penetrating the inlet.
5	<b>Wind Sensor, Met One Model 034A</b>	Analogue data logger and digital 8-port PC RS232 card-adaptor received and currently being tested in PC, and tested for data-acquisition. Analogue data logger used for Wind system calibration.
6	<b>Temp &amp; RH Probe, Vaisala</b>	Same as item 5, above.

PIU Detailed Status and Progress: Integrated size-segregated samples for chemical analysis (every 6th day)

	INSTRUMENT (Model)	PROGRESS
1	MOUDI, MSP Corp., 2 Rotating versions	Applied in EC/OC and Elemental studies. Currently 4 weeks of data acquired one week.
2	<b>One non-rotating MOUDI</b>	Applied in Organic PAH study. Currently 5 weeks of data acquired one experiment.
3	<b>Dual beam Aethalometer (Andersen)</b>	Continuous measurements are compared to those of ultrafine and fine measurement instruments, and associated with semi-volatile particle samples.

24-hour Integrated Samples

	INSTRUMENT (Model)	PROGRESS
1	<b>Hi-Vol (2)</b>	Installed by U.C. Riverside's PM-Center Core. Uses PM10 inlet and PUFF for s downstream of filter.
2	<b>PM10 and PM2.5 FRM Partisol</b>	Measurements paired with MOUDI, TEOM measurements.

**PIU Instrument Calibration Schedule**

Instrument Name	Units	Size Range*	Flow Rate	Calibration Frequency	Calibration Description	Period	Comments
SMPS	Microns	0.02 - 0.7	0.3 LPM	Monthly/per move	Standard PSL	Per Move	0.03, 0.21, 0.6 Micrometers
APS	Microns	0.6 - ~15-20	5.0 LPM	Monthly/per move	Standard PSL	"ibid"	0.67, 2.5, 3.6 Micrometers
TEOM	$\mu\text{g}/\text{M}^3$	PM 10	3.0 LPM	Monthly/per move	Comparative	"ibid"	Non-Volatile P
Partisol	$\mu\text{g}/\text{M}^3$	PM10/2.5	1.67/15.0 LPM	Monthly/per move	Comparative	"ibid"	Mass Balance Measurement
DataRAM	$\mu\text{g}/\text{M}^3$	PM 2.5	2.0 LPM	Monthly/per move	Comparative	"ibid"	Comparison wi Integrated Filter Measurements
MOUDI (Rotating)	$\mu\text{g}/\text{M}^3$	Mass/Size	30.0 LPM	per experiment	Comparative	"ibid"	Mass Balance Measurement
MOUDI (Non-Rot)	$\mu\text{g}/\text{M}^3$	Mass/Size	30.0 LPM	per experiment	Comparative	"ibid"	Mass Balance Measurement
Aethalometer	$\mu\text{g}/\text{M}^3$	Fine Mass	1 - 6 LPM	Monthly/per move	Comparative	"ibid"	Light transmission density
Vaisala Temp/RH 1	$^{\circ}\text{C}/\%$	NA	NA	NA	Sling Hygrometer	"ibid"	Inside PIU
Vaisala Temp/RH 2	$^{\circ}\text{C}/\%$	NA	NA	NA	Sling Hygrometer	"ibid"	PIU Roof
Met-1 Wind System	MPH, Direction	NA	NA	NA	Compass/Voltmeter	"ibid"	PIU Roof

\*NA = Not Applicable; \*\*ibid = Calibration period, same as SMPS.

### **3. Sampling in our First SCS Site (Rancho Los Amigos National Rehabilitation Medical Center)**

As mentioned in the previous paragraph, our PIU was installed at Rancho in August 3<sup>rd</sup>, 2000. We have continued our PM sampling at Rancho Los Amigos, in conjunction with ongoing human inhalation exposure studies to concentrated PM (these studies are part of our PM Center Toxicology core investigations). Our current sampling scheme involves 24-hour averaged, size-fractionated measurements of ambient and concentrated PM mass and chemical composition. Sampling is conducted approximately once per week.

During the period covering this progress report (July 15, 2000 to November 1, 2000), we have conducted 16 runs. In each run, consistent with our original Supersite proposal, we have used three collocated Micro-Orifice Uniform Deposit Impactor (MOUDI) to group PM into the following size ranges:

- <0.1  $\mu\text{m}$  (ultrafine particles)
- 0.15-0.35  $\mu\text{m}$  (accumulation mode, “condensation” sub-mode)
- 0.35-1.0  $\mu\text{m}$  (accumulation mode, “droplet” sub-mode)
- 1.0-2.5  $\mu\text{m}$  (“intermediate” mode)
- 2.5-10  $\mu\text{m}$  (coarse particles)

In addition to mass concentration, the following components have been measured for these size groups:

- a. inorganic ions (i.e., sulfate, nitrate, ammonium)
- b. trace elements and metals
- c. elemental and organic carbon (EC/OC) content
- d. concentrations of polycyclic aromatic hydrocarbons (PAH)



Ambient data are averaged over 24 hours, whereas data corresponding to concentrated PM are only averaged over two hours, as this is the typical duration of the human exposure experiments, conducted simultaneously with PM sampling. Analysis of these data is currently under way. We anticipate that the results from these measurements will be available within the next 2 months and will be included in the following quarterly progress report.

#### **4. Characterization of PAH Derivatives in PM<sub>2.5</sub> at a Source Site Impacted by Vehicle Emissions**

On September 15, 2000, we started our studies to characterize particle-bound PAH derivatives in a “source” site (Downey, CA), impacted primarily by vehicular emissions. These PAH derivatives originate from gas-phase two- to four-ring polycyclic aromatic hydrocarbons (PAH) reactions with hydroxyl (OH) radicals during the daytime and, if they are present, with nitrate (NO<sub>3</sub>) radicals during the nighttime (photolysis of NO<sub>3</sub>, formed from reaction of NO<sub>2</sub> with O<sub>3</sub>, prevents its build-up during the daytime). These radical-initiated atmospheric reactions will produce PAH derivatives more polar and less volatile than the parent PAH, which may then condense onto particles. Particle-associated PAH may be photolyzed and may react with ozone. Thus, polar particle-associated PAH derivatives may be expected to increase at sites receiving aged air masses in comparison with sites close to emission sources. This is significant because certain of these polar PAH-derivatives have been shown to be highly mutagenic in bacterial and human cell assay systems and carcinogenic in animal studies.

Naphthalene and methylnaphthalenes are abundant in emission sources such as diesel exhaust. These gas-phase PAH react with OH radicals (with lifetimes <1 day) and with NO<sub>3</sub> radicals to produce nitro-derivatives. The isomer profile of the 14 methylnitronaphthalenes (MNNs) formed from the OH radical-initiated reaction of the methylnaphthalenes is distinct from the profile of MNNs formed by NO<sub>3</sub> radical-initiated reaction. Thus, ambient measurements of MNNs may be used as a signature to identify the atmospheric chemistry that has occurred in an air mass, whether OH radical-initiated reactions, NO<sub>3</sub>

radical-initiated reactions or a combination of both. Our first SCS site, Downey, CA site is in an area heavily impacted by vehicle emissions and was chosen as a sampling site at which to characterize the polycyclic aromatic hydrocarbon (PAH) and nitro-PAH ratios and profiles resulting mainly from direct vehicle emissions.

#### Sampling Protocol

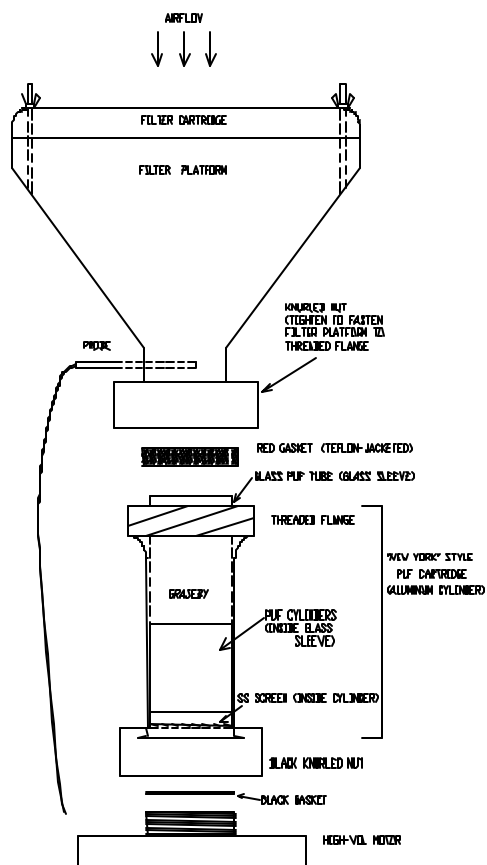
The gas-phase PAH naphthalene, 1- and 2-methylnaphthalene and biphenyl are sampled on replicate Tenax solid adsorbent cartridges at 100 ml/min using diaphragm pumps (Thomas) and mass flow controllers (Tylan General). The cartridges are capped and stored in a freezer until analyzed. The cartridges are spiked with deuterated internal standards, thermally desorbed, and the PAH quantified by gas chromatography/mass spectrometry.

The two-ring nitro-PAH, nitronaphthalenes, MNNs and 3-nitrobiphenyl, are sampled on polyurethane foam (PUF) samplers simultaneously collecting airborne vapor-phase "semivolatile" organic compounds and particulate matter. Each of the two standard high-volume samplers (Hivols) has been modified by the addition of a "New York Style" cylindrical aluminum cartridge for polyurethane foam (PUF) adsorbent plugs which are used for sampling vapor-phase organics. The samplers use a standard 8" x 10" Teflon-impregnated glass fiber (TIGF) filter upstream of the PUF adsorbent and operate at a relatively high flow rate of 20 scfm (560 liters per minute). The aluminum cartridges are lined with glass sleeves which contain the PUF adsorbent and are sealed with Teflon-jacketed gaskets (Figure 1). The sampler is housed in an anodized aluminum shelter and covered with an aluminum weather shield for outdoor service.

The TIGF filters (Pallflex T60A20) are precleaned by a 20-hour Soxhlet extraction with dichloromethane (DCM, Fisher Optima) followed by drying (60 °C, 3 hr) and a 20-hour Soxhlet extraction with methanol (MeOH, Fisher Optima). The pre-cut PUF plugs were obtained from S&W Plastics (Riverside, CA). Each sampling train consists of a front PUF plug (3 in. dia. x 3.5 in. long) and a back PUF plug (3 in. dia. x 1 in. long). The purpose of the back plug is to check for breakthrough from the main front plug. The PUF plugs are pre-cleaned by extraction in a large Soxhlet apparatus, first with DCM (20 hr) followed by drying (60 °C, 3 hr) and then by Soxhlet extraction with MeOH

(20 hr) and drying. The PUF plugs are wrapped in aluminum foil and placed in Ziploc bags inside glass canning jars and stored in the dark at -20 °C.

To be able to detect differences in daytime and nighttime atmospheric chemistry, the 24-hour sampling period is divided into two 12-hour day/night sampling intervals. The sampling is started at 7 AM, and at 7 PM the Hivols are shut down for 10 minutes to accommodate a change of the sampling media. Presently, the modified Hivols PUF samplers have been installed at the Rancho Los Amigos sampling site in Downey, CA. One 24-hour collection (10/19-20/00) has been completed and the PUF and filter samples have been stored in the freezer (20 °C) for upcoming extraction and analysis. Several day/night sample collections (one per week) are planned at Downey to fully characterize the PAH and nitro-PAH at this source site. Based on analyses of the gas-phase PAH and the nitronaphthalenes and methylnitronaphthalenes, the particles collected may be combined for analysis of particle-associated PAH derivatives.



**Figure 1.** Schematic of the modified Hi-Vol PM<sub>2.5</sub> sampler for collection of PAH derivatives

This study will continue at Downey until approximately January 20001. Subsequently, PAH and their derivatives will be collected following the same sampling scheme at a “receptor” site, which will be either the AQMD monitoring site in Riverside, CA or in Rubidoux, CA. These sites are approximately 10 miles apart and represent locations in which the urban plume has reached several hours after it was emitted. The effect of particle “aging” in the atmosphere of the Los Angeles Basin and its seasonal variations (i.e., differences between seasons of intense and low photochemistry) are also part of this investigation.

## **5. Size Distribution and Spatial Seasonal Variation of PAHs in the LAB**

One of the components of our Supersite project involves measurement of detailed size distributions of PAH in all of the Los Angeles basin sites proposed, during four seasons. Because the sites are located near sources and downwind from major sources, they provide an opportunity to determine whether partitioning occurs during transport across the Los Angeles Basin. Partitioning occurring during atmospheric transport would effectively alter the size distribution of the PAH and result in changes in their atmospheric transport and, more importantly, their deposition in the human respiratory system.

It has been established that, during collection on filters, semivolatile organic compounds (SVOC) such as low molecular weight PAHs can both adsorb on and desorb from particles during sampling, leading to positive and negative sampling artifacts, respectively. The use of a denuder ahead of a filter has been proposed as a means of reducing such sampling artifacts. However, removal of SVOC may alter the gas/particle thermodynamic equilibrium and potentially lead to distortions in the size distribution of the sample collected.

The effect of sampling artifacts on measurements of individual organics is not well understood as a result of these processes, in addition to the complexity introduced by the interaction of the various species present in ambient air. To evaluate if such sampling artifacts occur during sampling of the PAHs of interest in our studies, we designed a series of preliminary field experiments where samples were

collected using two co-located MOUDI impactors: One with the gas trapping system described below, and one without. Because the use of such trapping systems obviously increases the complexity of field operations, this series of experiments will help us decide whether such systems are indeed required in the determination of size-resolved PAHs.

Ambient aerosols were collected for 24-hr every 7<sup>th</sup> day during a five-week intensive campaign period carried out in Downey, starting on 28 September and ending on 27 October 2000. Collection was carried out at 30 LPM using a MOUDI impactor configured in the < 0.18  $\mu\text{m}$  (ultrafine), 0.18-2.5  $\mu\text{m}$  (accumulation), and coarse (2.5-10  $\mu\text{m}$ ) size ranges. A single channel annular denuder 24.2 cm long coated with XAD-4 resin was placed upstream of the MOUDI to trap semi-volatile organics while allowing transmission of the particles and collection on the Teflon filters of the impactor. To evaluate the occurrence of blow off from the impactor's backup filter, a cylindrical polyurethane foam plug (PUF) was placed in series behind it. With this configuration, collection artifacts, if present, may be eliminated or greatly minimized. In addition, for comparison purposes, two parallel samples (<2.5  $\mu\text{m}$ , and 2.5-10  $\mu\text{m}$ ) were also collected onto Teflon filters using a Partisol sampler.

Immediately after each sampling period, XAD-4 resin, Teflon filters and PUFs were stored in pre-baked amber glass containers and placed in a freezer. Over the next several weeks, all samples will be extracted and the 16 priority PAHs determined using an HPLC-fluorescence method developed in our laboratory. A comparison of the results obtained using the two sampling systems (with and without gas-trapping) will help us design a sampling system that is not, or is minimally susceptible to sampling artifacts.

## **6. Investigations of the Concentration and Source Origin of Allergens Present in Airborne Particulate Matter**

In September 2000, we have also started our studies to investigate the concentrations of PM-bound allergens in various locations of the Los Angeles basin. This investigation consists of two stages. The

first is a survey stage, during which  $PM_{10}$ -equivalent particle samples that have been collected on quartz fiber filters by low volume sampling at 12 cities that are under study as part of the USC Children's Health Study will be composited over the years 1994-1998 at each site and the 12 composite samples will be analyzed to quantify the total allergen exposure levels in each of these communities. This task has already started. These results will be used to identify locations with high allergen exposures in a way that will aid interpretation of the cause of allergic respiratory disease. The data will also provide information that will guide the subsequent siting (funded by EPA's Supersite program) of high volume samplers in 3 communities, the samples from which will be used to determine the nature of the sources that cause the allergen exposure.

At present, proteins are extracted from the Children's Health Study composite filter samples and the concentrations is determined by the bicinchoninic acid method (Stoscheck, 1990). Extracts are screened for the presence of relative allergenicity using slot-immunoblots, for the detection of IgE-binding allergens (Miguel et al., 1999). This detection method relies on use of human serum from a pool of allergic individuals and is capable of detecting allergenic proteins present in small respirable particles from man-made air pollution sources as well as pollen fragments that would not be detected by traditional pollen counting approaches. If enough sample material remains, *in vitro* ELISA (enzyme-linked immunoassay) – inhibition assays (AlaSTAT, Diagnostic Products Co.) will be used to measure the presence of allergens originating from specific source materials (e.g. trees or smoke from burning tree parts). These techniques for allergen detection and quantification in ambient samples have been demonstrated previously in Caltech research supported by the California Air Resources Board and the South Coast Air Quality Management District (Miguel et al., 1998). The resulting data will be useful in defining the spatial distribution of airborne allergens that can directly cause respiratory diseases such as allergies and asthma in a way that will assist interpretation of the differences in health status seen between communities in the USC Children's Health Study.

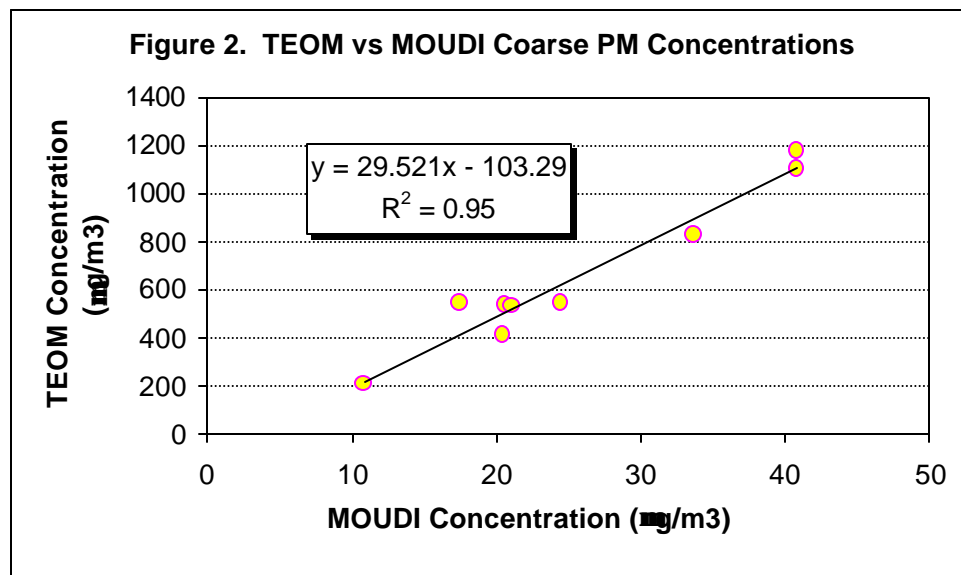
## **7. Development of a New High-Quality Continuous Coarse PM Monitor**

Measurement of coarse PM are inherently more complex and less precise than direct measurements of either PM<sub>2.5</sub> or PM<sub>10</sub> made with continuous or time-integrated monitors, as they are measured by the difference between collocated PM<sub>10</sub> and PM<sub>2.5</sub> samplers. Depending on the measurement method, PM<sub>2.5</sub> to PM<sub>10</sub> ratios and actual coarse PM concentration, mass concentration data for coarse PM may be substantially less precise than those for PM<sub>10</sub> or PM<sub>2.5</sub>.

As part of our Methods development section of our Supersite activities, we are currently developing a monitor that will yield precise, accurate, artifact-free coarse PM concentrations near-continuously (i.e., in intervals of 5 minutes or less). Towards this goal, we have developed a sharp cutpoint virtual impactor, operating at 50 LPM, of which 2 LPM are drawn through its minor flow, containing particles larger than 2.5  $\mu\text{m}$  in aerodynamic diameter, and enriched in concentration by approximately a factor of 23-25. These particles are then drawn through a TEOM (1400 A, Rupprecht and Patashnick), operating at a flow of 2 LPM. The virtual impactor is preceded by a perspective impactor/inlet that removes all particles above 10  $\mu\text{m}$  in aerodynamic diameter at 50 LPM. Two time-integrated monitors are sampling in collocation to the virtual impactor/TEOM system, a Microorifice Uniform Deposit impactor (MOUDI) and an R&P Partisol. The 2- to 3-hr time averaged coarse (2.5-10  $\mu\text{m}$ ) particle concentrations determined by means of the MOUDI and the Partisol are compared to the time-integrated concentration of the virtual impactor/ TEOM system. In addition, the 15-min mass concentrations of the modified TEOM are compared to these of an Aerodynamic Particle Sizer (3320, TSI inc.) sampling also concurrently to the rest of these monitors. The APS data represent volume rather than mass concentrations. Knowledge of particle density is required in order to convert the volume to mass concentrations. In these tests, the APS is used primarily to determine whether the 15-minute volume (APS) and mass (TEOM) coarse particle concentrations are correlated.



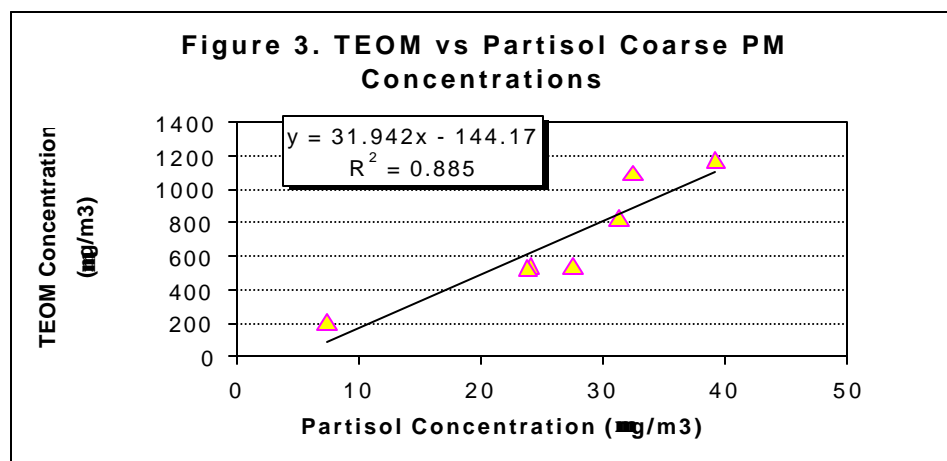
Results from these experiments are shown in Figures 2-5. Figures 2 and 3 show the comparison



between the 2-hour averaged TEOM concentration and the time-integrated concentrations of particle in the 2.5 – 10 µm range measured by the MOUDI and Partisol, respectively. The data plotted in Figures 2 and 3 show a very high correlation between the TEOM, MOUDI and Partisol concentrations ( $R^2$  of 0.95 and 0.89, respectively). The average TEOM-to-MOUDI concentration ratio was found to be  $24.9 (\pm 3.8)$ , while the TEOM concentrations were  $26.1 (\pm 4.2)$  higher than those of the Partisol.

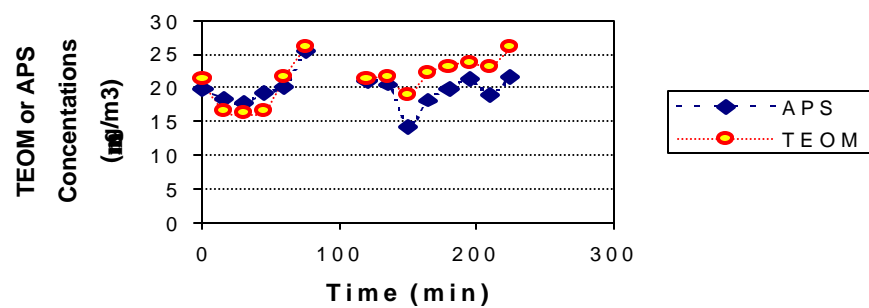
Figure 4 shows a time series of coarse (2.5 – 10 µm) particle concentrations measured over 4 hours by the APS and the modified TEOM. As the data of Figure 4 indicate the APS and TEOM concentrations track each other well.

The dependence of the TEOM-to-MOUDI or TEOM-Partisol ratio on the fine-to-coarse PM

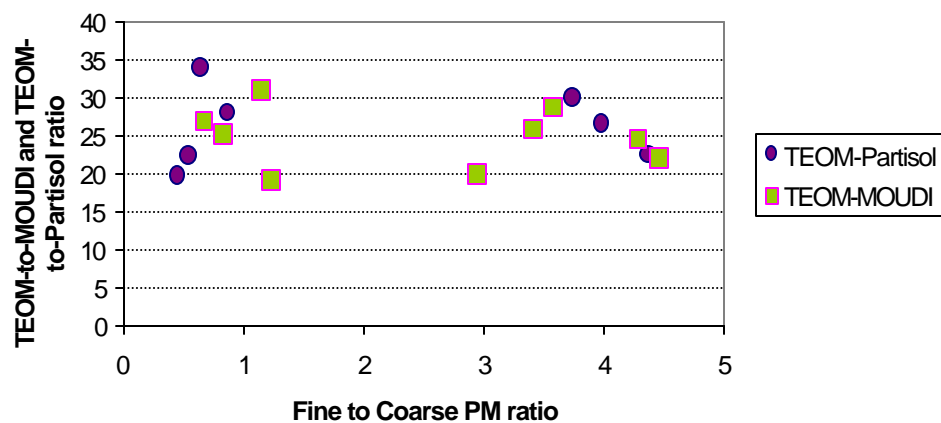


ratio is shown in Figure 5. Although preliminary in nature, these results do not show a significant dependence of the ratio of the TEOM-to-time integrated sampler concentrations on the relative fractions of fine-to-coarse PM. The above results indicate that this modified version of the TEOM could provide very accurate continuous measurements of coarse PM in short time intervals. Coarse concentrations measured by the modified TEOM should be divided by 25 (i.e. the ideal enrichment factor of the virtual impactor preceding the TEOM). The resulting error according to our data so far would be on the order of  $\pm 10\%$ .

**Figure 4. Time-series of TEOM and APS Coarse Concentrations**



**Figure 5. Dependence of TEOM-MOUDI and TEOM-Partisol Ratio on Fine/Coarse PM ratio**



## **8. Measurement of the Spatial and Seasonal Variation of Ultrafine PM in the LAB and their Relation to Sources**

The purpose of this research is to determine whether ultrafine particle concentrations are affected mainly by local sources rather than having a uniform spatial distribution. Starting in October of 2000, the Air Resources Board of California placed 12 Condensation Particle Counters (TSI CPC, 3022) in each of the USC Children's Health Study sites. These sites include Long Beach, Fontana, Lake Elsinore, Upland, and Rubidoux Mira Loma, Glendora and the University of California Riverside campus.

Custom-made aluminum inlets were fabricated to draw the ultrafine ambient aerosols into the CPC, which were placed inside the existing monitoring stations in the communities of the CHS, operated by ARB. Ultrafine PM are sampled at a flow rate of 16.7 LPM, of which 0.3 LPM is diverted to the CPC, whereas the remaining 16.4 LPM is exhausted. The reason for this modification was based on our experimental observations which indicated that if ultrafine PM is drawn at the nominal flow rate of the CPC (i.e., 0.3 LPM), approximately 60-80% of the ultrafine particles are lost before they reach the CPC, mainly due to diffusional deposition on the aluminum inlet walls. In order to avoid these losses, we decreased the residence time of ultrafines in the aluminum tube by using a larger pump to draw the particles at 20 LPM, of which only 0.3 LPM is drawn through the CPC. These measurements are under way.

As part of our data analysis, the 5-min, 1-hr and 24-hour averaged ultrafine number concentrations measured in each site will be correlated. Of particular note will be the degree of correlation obtained between ultrafine counts in sites relatively close to each other that will confirm that importance of local sources on ultrafine PM concentrations. Multiple regression will be performed between the 1-hr and 24-hour average number concentrations and distance from sampling site to a freeway. We anticipate that a strong negative correlation exists between ultrafine PM concentrations and distance to freeways. We will also test the hypothesis of whether the majority of ultrafine particles are from nearby (<500m), fresh emissions sources. Small particles with aerodynamic diameters  $<0.1 \mu\text{m}$  ( $\text{PM}_{0.1}$  or "ultrafine" particles) are believed to coagulate into larger particles within a short distance of their emissions. If this

is true, their numbers should increase in short duration spikes and be consistent with wind directions favoring nearby emitters. From 5-min spikes over longer-term averages of ultrafine particles as small as 0.003  $\mu\text{m}$  measured with the Condensation Particle Counter, we will estimate the incremental mass contributed by nearby sources.

## **9. Progress on Site identification**

A key feature of our Supersite activities was the ability to conduct state-of-the-art measurements of the physicochemical characteristic of PM in different locations of the Los Angeles Basin (LAB). The LAB suffers the most serious photochemical smog impacts in the nation including the highest ambient air concentrations of ozone and particulate matter. The major goals of the site selection were to optimize the scope, importance and magnitude of the information to be obtained, and to facilitate the use of the data for health effects research being conducted under the Southern California PM Center. In selecting specific locations for the principal Supersite facility over a five-year period, it was important to account for these geographical, seasonal and long-term air quality patterns. Similarly, attention was paid to the need for “representative” sampling of the full spectrum of air pollution phenomena in the region with particular attention to the production, transport and impact of PM. An additional key issue in site selection is the existence of the USC Children’s Health Study, a 10-year, 12-community study supported by the ARB and HEI. About 4000 school children living in 12 communities with differing levels and types of pollution have been under study since 1993. In making our final proposed site selections we have also taken into account logistical and infrastructure considerations relevant to the implementation and support of the facility including the location of existing agency-sponsored air monitoring stations which offers the availability of secure sites. Finally, we have considered the scientific goals and hypotheses of the participating investigators and the needs of the collaborating health effects researchers affiliated with the EPA STAR PM Center based at UCLA.

We have proposed a 2.5-year repeating cycle of measurements at five locations. Each location will be sampled during a period of intense photochemistry (defined approximately as May – October) and low photochemical activity (defined as the period between November – April) We have identified the following 5 locations as ideal candidates for the principal Supersite site.

1. Rancho Los Amigos Medical Center (Alameda Corridor)
2. Long Beach (coastal site)
3. Rubidoux (eastern region, SCAQMD speciation site)
4. Azusa (SCAQMD PM monitoring site; inland valley)
5. Riverside (eastern region site, operated by University of California Riverside)

Sampling in our Rancho Los Amigos site started in May 2000. Part of this period was used as a “shakedown” period, in which problems with the PIU set-up and instrument operation were identified. As of August 2000, this site is used officially as our first Supersite site and we anticipate that sampling will continue in this location until January 2001. In February of 2001 we will move the PIU to Riverside, where we will conduct our Supersite activities until June 2001. We will subsequently move to Rubidoux and continue our Supersite measurements until November 2001. In December of 2001 we anticipate moving our activities to Long Beach, where we will sample until May 2002, and we will subsequently move to Azusa during the intense photochemical period (May – October) of year 2002. At that time we will repeat our measurement cycle, this time starting with Rancho Los Amigos (November 2002 – April 2003), Riverside (May 2003- October 2003), Azusa (November 2003 – April 2004), Long Beach (May – November 2004).

We have already confirmed the sites of Riverside and Rubidoux and received authorization from Real Estate Revenue (proprietor of the Rubidoux site) and the department of Agricultural Sciences, University of California, Riverside (proprietor of the Rubidoux site) to use both sites for the calendar year 2001. In collaboration with the Office of Applied Science and Technology of SCAQMD we have identified 3 candidate sites in the area of Azusa and we are in the process of selecting the optimum of the three on the basis of logistics, convenience, security and availability of power lines. Finally, and in close collaboration with the Monitoring and Laboratory Division of the California Air Resources Board, we are pursuing our fifth site in the Long Beach area. We have identified a candidate site in the Wilmington High School area and received permission for the high school lot use the schoolyard for installing the ARB and our monitoring trailers. We will coordinate our measurements with those

conducted by ARB, which focus on measurement of air toxics in environments where children spend the majority of their time (funding for these monitoring activities comes from Senate Bill 25). Our activities will be thus leveraged with the concurrent ARB measurements, which will provide us with information on organic air toxics (mainly in the vapor phase) currently not measured by our Supersite, but which are important in supporting the toxicological and in vitro evaluation health studies that we will be conducting in our Supersite locations.

## **10. Progress with Data Management Plan**

**Data handling Summary:** The budget for acquisition of a data-logger and software has been approved. To date, manual data transfer processes have been used, except for the SMPS, APS, and DataRAM monitors. Automatic data acquisition, storage, transfer, and management plan being developed and tested for SMPS and APS.

### **1. Scope**

This plan describes the type of data that will be generated in SCS, the characteristics of these data, the process of handling these data, and the hardware that needs to complete such a task.

### **2. Description of Database**

The SCS consists of research and service cores including analytical chemistry, dosimetry and biostatistics service cores within the Center to facilitate investigations in research cores in exposure, toxicology, epidemiology and particle concentrator studies. Data generated from these research activities are generally classified into three categories: primary raw data, secondary processed data, and publication-ready data, as illustrated in Figure 1.

## **2.1 Primary Raw Data**

The primary raw data are those originally generated from data loggers, monitoring instruments, analytical equipment, and those written in field logbooks and lab notebooks, inserted in primary forms without complicated processing. These data are present in different formats, depending upon the origin of data acquisition. They can be written records in field logbooks and lab notebooks, questionnaire, printout and electronic records generated from data loggers and monitoring instruments. Quality assurance and quality control are usually required to maintain precision and accuracy of data at the best achievable level. These data will be the primary sources of further statistical and mathematical treatments.

The major sources of these primary raw data will be generated from the Particle Instrumentation Unit (PIU) of the SCS, consisting of aerosol instruments shown in Table 1. The table details the units, signal format and process, path or media of transfer, duration, and type of analysis. These data are to characterize air pollution components and associated information in LA Basin. These data will be directly generated from the instruments or require data loggers to transform analog signals into electronic data. An on-site data acquisition computer, located in mobile PIU, will be needed to handle and preliminarily process these primary raw data, as outlined in Figure 6.

An additional procedure is required for those instruments generating sampling mediums (such as air filters), not electronic data for air pollution components. These sampling mediums are to be analyzed by in-house or other analytical labs. Table 2 highlights the in-house analytical methods that will be used for chemical analysis of PM samples collected by the SCS. . All information related to analysis of the samples is considered as primary raw data as well. The analytical results will be transferred to the central server computer, which will be linked with sampling records associated with original conditions taken in PIU.

### ***Size of SCS Primary Raw Data***



It is anticipated that large amount of data will be generated from the SCS PIU instruments during the next 4 years study period. Table 3 is an initial estimate of the size of the databases. It is estimated that a total of more than 7 gigabytes of primary raw data will be generated from PIU instruments.

### ***Description of Data Acquisition System Components***

Table 1 lists the electronic signal or sample type (requiring further analytical analysis) generated by each PIU instrument. The MOUDI's will generate filter samples for gravimetric analysis and/or chemical analysis (e.g., for Particle associated elements, ions, and organic compounds). Additionally, the Partisol Dichotomous Coarse and PM2.5 monitor samples onto filter media for gravimetric analysis. The mass and chemical data generated by these instruments will be recorded by hand onto data sheet and then entered into individual spreadsheets. The electronic flow/volume data is digitally recorded to an on-line system.

The remaining instruments of the PIU generate electronic particle or gas data, consisting of either/or an analog or digital signal. The analog signals are generated by the Wind instruments (Met-One), the thermohygrometric instruments (Vaisala), and the Dasibi Ozone and Carbon Monoxide gas instruments. These instruments require an analog-to-digital multichannel (9-input) system (supplied by Met-One instruments), specially designed to interpret pulsed multidirectional wind signals, but also able to read general pulsed analog signals. The signals from all instruments are coupled into a single signal that is supplied through a RS232 serial cable for digital transmission of the data.

The remaining particle instruments and APS NO<sub>x</sub> gas analyzer generate a digital signal with RS232 output. A multi-cable (8) adaptor board (Keithley Products), installed into a dedicated Data Acquisition PC, has the capability of accessing multiple digital signals simultaneously, including that supplied by the A/D Met-One Data Logger.

The Data Acquisition Computer operates continuously, and communicates with all gas and particle monitors at a rate determined by the software (including drivers) typically supplied by each respective particle/gas instrument manufacturer.

## **2.2 Secondary Processed Data**

The secondary processed data contain essential variables of the records from primary raw databases transferred from a variety of studies for environmental sampling (also, for epidemiology, and in vitro and in vivo investigations). The essential variables include those for where and when are the primary raw data collected, who (which study in SCS) collects the data, what characteristics and observation values of these raw data, and how the data are collected. The essential variables should be able to trace back from the primary raw databases. Table 4 outlines more details about these variables. The initial estimate of the size of the secondary processed databases is about 1/3 of the primary raw databases, i.e., about 2.3 gigabytes. These data will be mainly stored in the central server that can be connected to outside of the SCS through the Internet.

## **2.3 Publication-Ready Data**

Publication-ready data are abstracted and carefully evaluated from secondary processed data through statistical or mathematical modeling treatments. They will be those used in publication, internal and external reports, and other circulation documents. These data will be scientifically defensible.

**Table 1. UCLA SCS PIU Routine Raw Data Acquisition Summary**

Instrument Description			Signal		Path/ Media	Sample Duration
Name	Units		Format*	Process**		
1	SMPS	Particles/cm <sup>3</sup> and µg/M <sup>3</sup>	Digital	On-Line/Integrated	Electronic	5 min
2	APS	Particles/cm <sup>3</sup> and µg/M <sup>3</sup>	Digital	On-Line/Integrated	Electronic	5 min
3	TEOM	µg/M <sup>3</sup>	Digital	On-Line/Integrated	Filter/Electronic	10 min
4	Partisol	µg/M <sup>3</sup>	Digital	Sample	Filter	24 hours
5	DataRAM	µg/M <sup>3</sup>	Digital	Automatic	Electronic	10 sec
6	MOUDI (Rotating)	µg/M <sup>3</sup>	N/A	Sample	Aluminum Substrate	24 hours
7	MOUDI (Non-Rot)	µg/M <sup>3</sup>	N/A	Sample	Filter Substrate	24 hours
8	Aethalometer	µg/M <sup>3</sup>	Digital	Continuous	Qtz-Filter/Electronic	10 min
9	Vaisala Temp/RH 1	Deg-C, %RH	2-Analogs	On-Line/Continuous	Electronic	1 hour
10	Vaisala Temp/RH 2	Deg-C, %RH	2-Analogs	On-Line/Continuous	Electronic	1 hour
11	Met-1 Wind System	mph/N,S,E,W	2-Analogs	On-Line/Continuous	Electronic	1 hour
12	APS NOx Gas	ppb	Digital	On-Line/Continuous	Electronic	1 hour
13	Dasibi CO Gas	ppm	Analog or Digital	On-Line/Continuous	Electronic	1 hour
14	Dasibi Ozone Gas	ppb	Analog	On-Line/Continuous	Electronic	1 hour

\* Signal To Computer

\*\* Data is Automatically transmitted to Data Acquisition System, or Sample is collected for gravimetric and/or chemical analysis

\*\*\* Grav = Gravimetric; Elem = Elemental, BC = Black Carbon, T = Temperature, RH = Relative Humidity, WS = Wind Speed, Dir = Direction

I = Integrated, C = Continuous, Org = Organic

**Table 2. SCS Analytical Methods**

Analysis_Method_Code	Analysis_Method_Desc
-	-----
CAR	Cartridge
FIL	Filter
	Gas Chromatography/Mass Spectrometry
GCM	(GS/MS)
GRA	Gravimetry
HPL	High Performance Liquid Chromatography

ICG	Ion Chromatography
IMP	Impactor
TOR	Thermal Optical Reflectance
TUB	Tube
XRF	X-Ray Fluorescence

**SCS Target Analytes please delete this table; it is not necessary and it misses inorganic ion ad trace elements.**

Analytes_Code	Chemical Agent
-----	-----
NAP	naphthalene
ACY	acenaphthylene
ACE	acenaphthene
FLU	fluorene
PHE	phenanthrene
ANT	anthracene
FLT	fluoranthene
PYR	pyrene
BAA	benzo(a)anthracene
CRY	chrysene
BBF	benzo(b)fluoranthene
BKF	benzo(k)fluoranthene
BAP	benzo(a)pyrene
IND	indeno(1,2,3-cd)pyrene
DBA	dibenz(a,h)anthracene
BGP	benzo(ghi)perylene
OC	Organic carbon
EC	Elemental carbon
CC	Carbonate carbon
TC	Total carbon

**Table 3. Estimate of the number of records generated from PIU Instruments**

Instrument	Samples per day	No. of days	No. of Years	No. of Measures	No. of Stages	No. of Records/Year	Summary
SMPS	288	365	4	1		140160	4 data points per hr
APS	96	365	4	1		140160	4 data points per hr
TEOM	48	365	4	1		70080	2 data points per hr
DataRam	288	365	4	1		420480	12 data points per hr
MOUDI-1	1	60	4	5	5	1500	Every 6 days, agents include particle ma
MOUDI-2	1	60	4	10	3	1800	Every 6 days, PAHs
MOUDI-3	1	60	4	2	5	600	EC and OC (every 6 <sup>th</sup> day)
MOUDI-4	1	60	4	10	5	3000	Metals (every 6 <sup>th</sup> day)
Aethalometer	48	365	4			70080	
High Vol			60			60	
PM10/PM2.5 FRM	2	365	4			2920	2 filters per day
Gas Analyzer	24	365	4	3		105120	24 samples per day for NO, NO2, CO
Meteorological data	288	365	4	4		1681920	5 min avg. time give 12 data point per da direction, speed, relative humidity, and te
Total						2928820	

If each record contains 250 bytes (a crude estimate), then the database will need 2928820\*250 = 7,322,050,000 bytes  $\approx$  7.3 gigabytes.

#### Essential Variables of Secondary Processed Data

Variable Category	Variable Name	Example/Note
Where	Site_Identification	Ex: ES2LUSCAxxxx, where xxxx represents LA site codes: Riverside, RBDX for Rubidoux, LNGB for Long Beach, DV AZSA for Azusa. Additional information may include latitude, elevation, and county of the site.
When	Study_Date	Ex: 20001101
	Duration	Ex: 6 hr
Who	Data_Source	Ex: PIU or Analytical Chemistry Lab
What	Record_ID	Ex: PIU200011010001-1
	Substance	Ex: PM2.5, OC, BaP, metals, NO
	Observation_Value	Ex: 100
	Observation_Units	Ex: $\mu\text{g}/\text{m}^3$

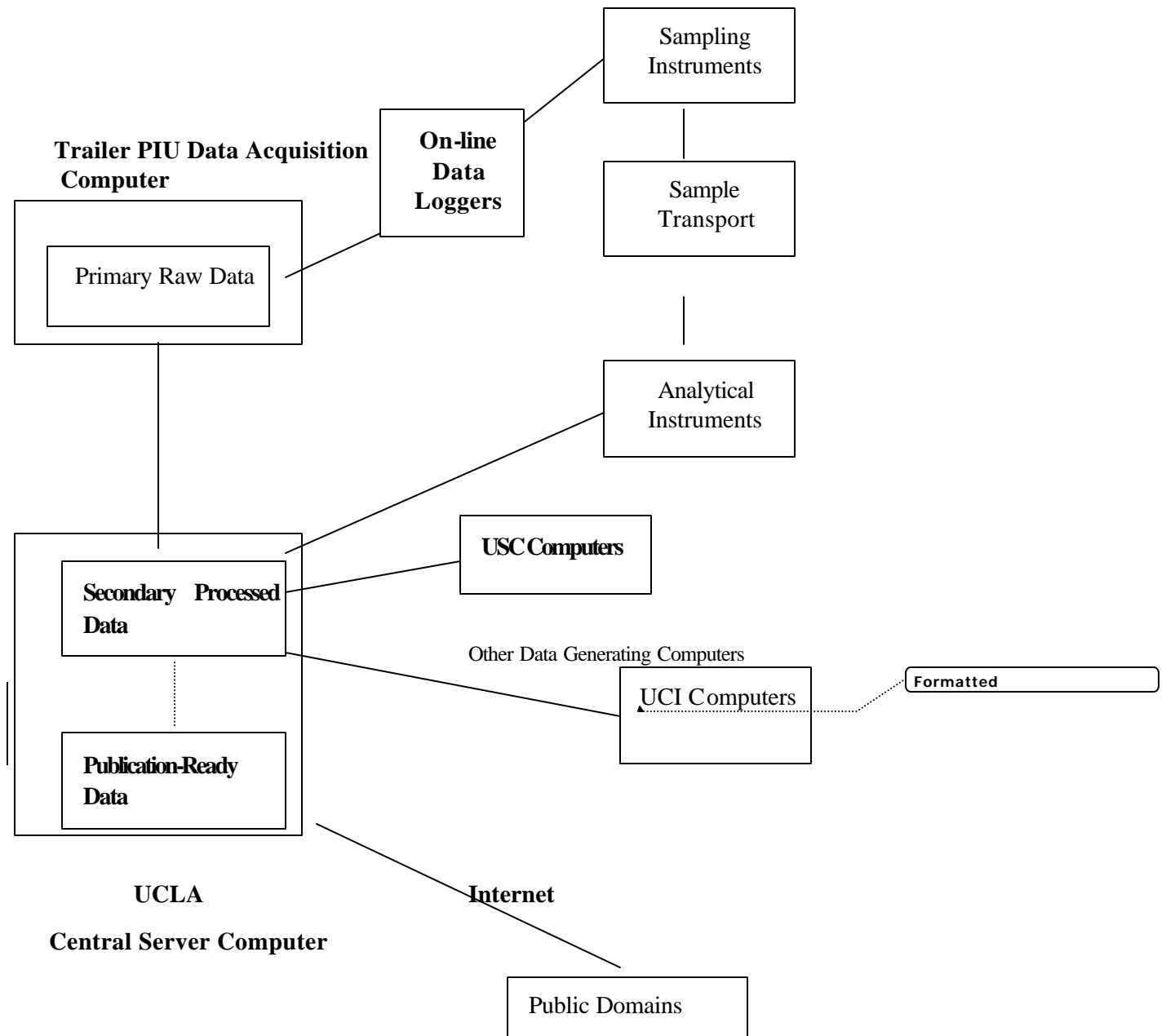
**How**

Sampling\_Method  
Analysis\_Method

Ex: MOUDI  
Ex: Gas Chromatography/Mass Spectrometry (GS/MS)

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**Figure 6. Data Flow between Sampling Instruments Computers**



## **References**

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